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[illegible] Report [illegible]

Thermal Stability of Ethylenedinitrilotetraacetic Acid and Its Salts

Part 1 - A Literature Survey

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CONTENTS

ABSTRACT

From the standpoint of boiler-wall corrosion prevention, preliminary studies at this Laboratory and at the Naval Ship Research and Development Center have indicated that a chelating agent, ethylenedinitrilotetraacetic acid (H_4EDTA), in conjunction with lithium hydroxide is preferable to the low-phosphate control treatment presently being used by the Navy. To elucidate the corrosion-inhibition mechanism in the lithium hydroxide-$EDTA^{4-}$ system, we must know the rate and the mechanism of $EDTA^{4-}$ decomposition in aqueous solutions under conditions of high-pressure boiler operations. As a background for investigations at this Laboratory of the solid phase and solution phase decomposition of $EDTA^{4-}$ at high temperatures, the available literature has been examined and pertinent facts related to the lithium hydroxide-$EDTA^{4-}$ system are reported. The general properties of $EDTA^{4-}$ chelates are reviewed first. Although a considerable amount of information is available related to the use of alkali-metal hydroxides and $EDTA^{4-}$ solutions for hard-scale removal and corrosion prevention, no studies have been reported on decomposition products from aqueous $EDTA^{4-}$ solutions heated under pressure to high temperatures. The qualitative investigations of the thermal decomposition of solid H_4EDTA and its metal salts fail to fully identify the volatile products and residues formed at temperatures near those of boiler operations.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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Introduction

For treatment of steel at elevated temperatures in steam power generator boilers, lithium hydroxide has recently been shown to be an effective additive (1,2). However, the deposition of lithium phosphate on the boiler walls prevents the simple substitution of lithium hydroxide for sodium hydroxide in the conventional Navy low-phosphate treatment for boiler water (3). To prevent hard scale formation by alkaline earth ions, which are always present in boiler water, addition of a soluble organic chelating agent in place of the phosphate was proposed for the lithium hydroxide system. Preliminary studies in capsule systems at this Laboratory and in model boilers at the Naval Ship Research and Development Center have indicated that one chelating agent, ethylenedinitrilotetraacetic acid (H_4EDTA), in conjunction with lithium hydroxide, is preferable, from the standpoint of prevention of boiler wall corrosion, to the low-phosphate control treatment presently being used by the Navy (3).

To elucidate the corrosion-inhibition mechanism in this preferred system of lithium hydroxide and $EDTA^{4-}$, it is necessary to know the stability of the organic chelating agent, the state of aggregation of lithium ions, iron ions and $EDTA^{4-}$ ions at the pH and temperature conditions of boiler operation. Examination of the available literature has revealed many pertinent facts related to the lithium hydroxide-$EDTA^{4-}$ system and these are reported herein as a background for studies at this Laboratory of the solid phase and solution phase decomposition of $EDTA^{4-}$ at high temperatures. From these studies, the function of the chelating agent may be determined, and new chelating materials of the proper stability recommended for future screening tests.

General Properties of $EDTA^{4-}$ Chelates

Aqueous solutions of metal ions contain complexes because of the polar nature of the water molecules and the ionic charge of the metal ion. The spatially oriented water molecules must be replaced if complex formation takes place with ligands other than the solvent. Many interrelated factors influence the selectivity and the stability of complexes: (a) the nature of the atoms concerned in bond formation; (b) the base strength of the ligand which may be an anion or neutral molecule with basic properties; (c) the stereochemistry of the complex formed; and (d) any contributions due to resonance. Another important consideration is the "chelate effect"; the more points of attachment there are between a ligand and a metal ion, the more difficult it will be for the metal ion to break all the bonds and move away before the chelate can reform. Thus, the stability constants of the iron(II) complexes with ammonia, ethylenediamine and ethylenedinitrilotetraacetic acid increase as the points of ligand attachment increase from 1 to 2 to 6, respectively (Fig. 1).

Formation constants of some 1:1 metal-$EDTA^{4-}$ complexes at 20°C in 0.1M KCl (4) are listed in Table I. In general, for a given ligand, complexes are least stable for monovalent cations; the stability increases with increasing cationic charge and decreasing ionic radius (see Table I: Li^{+} vs. Fe^{3+} and Fe^{2+} vs. Fe^{3+}). Since a ligand may be considered a base, at sufficiently low pH the molecule may become extensively protonated and its complex forming ability reduced. $EDTA^{4-}$ is nearly equal to the total H_4EDTA added when the pH is between 11 and 12 (5).

Ringbom (6) reported that the optimum pH for $EDTA^{4-}$-complex formation is the value at which the metal complex has an apparent stability constant of 10^8 (Table I). Accordingly, at pH 3 the iron(III) complex-formation is complete within one part in 10^9 when the free $EDTA^{4-}$ concentration is 2×10^{-6}M. If the pH of the solution is increased, another important factor that must be considered is the hydrolytic equilibria.

Although the stability constants of Fe(III)- and Fe(II)-$EDTA^{4-}$ indicate relatively high stability (Table I), the iron(II) or iron(III) hydroxides may precipitate if the solution is made too alkaline. Consequently, for a 10^{-3}M Fe(III)-$EDTA^{4-}$ solution which is 10^{-3}M in free $EDTA^{4-}$, precipitation of $Fe(OH)_3$ [pK_s = -42.7 (7)] should begin when the pH reaches about 8 or greater. However, under the same conditions, precipitation of $Fe(OH)_2$ [pK_s = -15.2 (7)] should begin only when the pH reaches about 14 or greater. Since the reported K_s values vary (4), the calculated value of pH will depend on the choice of K_s used. Consequently, the pH values are only used to illustrate the differences between Fe(II) and Fe(III) solubilities.

Of the $EDTA^{4-}$ groups that are involved in metal-complex formation, the last one, or sometimes the last two, binds relatively weakly. This makes it possible for one or two of the coordination sites around a metal ion to be occupied by water molecules which can lose protons (hydrolyze), giving rise to complexes with $Fe(OH)^{2+}$ or $Fe(OH)_2$ chelated to $EDTA^{4-}$. Both of the resulting complexes have lower stability constants than the metal ion complexes which would be present in solutions at lower pH values. Consequently, under ideal conditions at

20°C, a pH 11 solution containing Mg^{2+} and $Fe(OH)_2^{+}$ ions would have conditions conducive to complex formation between Mg^{2+} and $EDTA^{4-}$, but the iron would be precipitated as the hydrous oxide. The calculated values for the formation constants of $Fe(OH)_2$-$EDTA^{4-}$ and $Fe(OH)_3$-$EDTA^{4-}$ corroborate the expected solubility of Fe(II) and insolubility of Fe(III) at high pH values (Table I). Temperature as well as concentration and pH will affect the stability and the nature of the resulting chelate.

Aqueous Solutions of $EDTA^{4-}$ Used in Boilers

Aqueous solutions of ethylenedinitrilotetraacetic acid (H_4EDTA), its salts, and derivatives are used extensively as reagents in analytical chemistry (8). The patent literature also abounds with industrial uses. However, no thorough studies of the high temperature and pressure stability of these aqueous solutions have yet been reported.

Acting similarly as the polyphosphates, $EDTA^{4-}$ suppresses the effect of hard water ions by complexing ions such as Ca^{2+} and Mg^{2+}. Unlike the insoluble phosphates, the $EDTA^{4-}$-chelated ions usually remain in solution; the soluble complexes of the undesirable ions are easier to remove than the solid phosphates. Consequently, the literature contains many reports of the successful use of H_4EDTA, its salts, and derivatives, as well as other similar chelating agents, for cleaning boilers which are scaled (9). To lessen the cost of the chemical cleaning, the ED[illegible]utions can be treated with acid to recover H_4EDTA for reuse. For general cleaning of utility boilers, salts of $EDTA^{4-}$, such as the ammonium or sodium salt, remove magnetic iron oxide less effectively than hydrochloric acid chemical cleaning; furthermore, the $EDTA^{4-}$ treatment is more expensive than the hydrochloric acid treatment (10).

Goldberg and Arrhenius (11) used $EDTA^{4-}$ solutions to determine the dissolution rate of several ground samples of minerals (3.2 - 10μ equivalent diameters); the mineral sample was suspended in 5% "EDTA" buffered to a pH of 8 with ammonia and agitated for 2 hrs. at 100°C. A progressive decrease of dissolution rate with time was noted in most cases. The range of dissolution was from 17 to 470 mg m^{-2} hr^{-1} for the minerals tested. The characteristic of $EDTA^{4-}$ to dissolve minerals was utilized by Kajanne (12) who found that the iron content of boiler water without $EDTA^{4-}$ was 2.9 - 3.7 mg/l. When 1 kg of EDTA/80 tons of steam was fed to the low pressure test boiler, the iron content of the boiler water became 11.5 to 27.5 mg/l. Kajanne estimated that 1 kg of EDTA would remove 1.2 kg of scale from the boiler (12). By formation of a Fe^{2+} - $EDTA^{4-}$ complex, iron(II) ions were assumed to have been prevented from forming a precipitate. Since the residual hardness of the feed water may inactivate the $EDTA^{4-}$, the feeding rate determined by Kajanne may not be ideal.

Münz (13) reported that alkali-metal salts of ethylenedinitrilotetraacetic acid and nitrilotriacetic acid are suitable for treating hard water to prevent the formation of precipitates, but Bersworth (14) noted that these compounds were unsuited for treating boilers to remove and prevent scale formation. Although Na_4EDTA solutions will dissolve freshly precipitated calcium salts, it will not dissolve or loosen hard incrustations of calcium, magnesium, and iron salts.

found inside boiler tubes. By adding a relatively small proportion of alkali-metal hydroxide or a water soluble alkali-metal salt of a comparatively weak water soluble acid, scale formation was loosened and dissolved at the boiling point of the cleaning solution. Bersworth reported that, once the scale had been removed, the tubes of the boiler could be kept free from scale by adding an "alkylene polyamine tetra (or higher) acetic acid" and an alkali-metal hydroxide to the feed water. A typical aqueous solution, which was recommended by Bersworth to remove hard, thick scale from boilers without damage to tubes and to prevent further scale formation, consists of an alkali-metal salt of an "alkylene polyamine tetra (or higher) acetic acid" (0.1 to 2% by weight), an alkali-metal hydroxide (10 to 25% by weight), and a water soluble weak acid to give a solution of pH 8.5 or greater.

If iron oxide and carbonaceous materials are present, a more elaborate system for removing scale at 90°C consists of water (795 pts.), 50% sodium hydroxide solution (210 pts.), Na_2H_2EDTA (20 pts.), triethanolamine (100 pts.), sodium hydrosulfide (30 pts.), alkylaryl benzene or naphthalensulfonate (0.125 pts.), and Kerosene (293 pts.) (15). Under the conditions used, Fe(III)-triethanolamine complexes are reported to remain soluble and to have their highest stability at a pH range 13 to 14.

In cane-sugar factories, hot 2 to 5% $EDTA^{4-}$ solutions (pH between 6 and 11) have been used to descale brass evaporator heating surfaces. The scale usually consists of calcium salts with a small proportion of magnesium salts, and the common anions are sulfate, phosphate, silicate, and anions of organic acids. Silica, silicates and iron oxides are not removed by the $EDTA^{4-}$ treatment (16,17). When the used $EDTA^{4-}$ cleaning solution is acidified with sulfuric acid to pH [illegible], calcium sulfate precipitates, the pH is then increased to 6 and the solution is ready for reuse. Although the magnesium content of the solution builds up, insoluble H_4EDTA can be recovered for reuse by lowering the pH to 1.5. Under favorable conditions less than 2% loss of H_4EDTA per week was reported (17).

The calcium sulfate, which is of paramount importance in sugar factory evaporators, remains soluble in $EDTA^{4-}$ solutions regardless of pH, and its solubility is not influenced by the presence of fluoride, phosphate, carbonate, or oxalate, all of which form sparingly soluble calcium salts. An activation energy of 4.0 kcal mole was reported for the process of dissolving calcium sulfate in $EDTA^{4-}$ solutions (18). Since the activation energy is relatively low and the rate of solution is increased by increasing the flow of liquid past the scale, the rate controlling step of calcium sulfate dissolution is indicated to be a physical rather than a chemical process. For calcium sulfate scales, the rate of cleaning becomes independent of pH above [illegible] and therefore indicated, and now confirmed, that the use of very alkaline $EDTA^{4-}$ solutions for cleaning evaporators is not necessary ([illegible]). Schmidt and Wiggins ([illegible]) noted that the oxide film on brass evaporator tubes was dissolved, and the metal was left perfectly clean and bright. [illegible] the evaporator was put in service, the metal remained clean and bright for several weeks, whereas acid-cleaned tubes were [illegible] film very rapidly. The removal of the oxide layer from the [illegible] affect the subsequent deposition of scale. [illegible] solutions are boiled, sometimes at reduced pressures, no mention of the thermal decomposition of the reagent is reported. In fact, the reports usually state that the highly alkaline Na_4EDTA solutions are stable to boiling.

The large amounts of the Na_4EDTA needed to effect the cleaning is a major disadvantage. For cleaning the sugar evaporator tubes, the weight of Na_4EDTA necessary to completely dissolve the scale is about twice the weight of the scale (18). For keeping the tubes clean, Schmidt and Wiggins (19) suggested the addition of Na_2H_2EDTA to the "juice line" from time to time.

In a study of the dissolution of iron, zinc and cadmium, at room temperature and at a pH of about 2, King and Hillner (20) reported the effect of complexing or chelating agents on the inhibitor properties of dilute dichromate solutions. The authors used cylinders of the metals rotating at 15,000 cm/min at temperatures of 25° to 28°C. Saturated solutions of H_4EDTA with 0.01M dichromate showed some increased inhibition of dissolution as compared to solutions without H_4EDTA. With dichromate present the iron acquired a light yellow film, the cadmium a light brown film; both rubbed off easily with alcohol. The authors consider two views for the function of complexing or chelating agents: first, they prevent precipitation of oxides or hydroxides by forming soluble complexes with ions not involved in forming the tightly adherent film of impervious oxide; or second, these reagents act to clean the surface of air-formed, less protective films, thus allowing free access of dichromate ion to be adsorbed. Compositions for inhibiting corrosion of ferrous metals have been reported in which a combination of chromate and a sequestering agent (Na_4EDTA), which is capable of complexing iron(II), are used (21,22). However, information concerning corrosion of steel indicates that the chromate is necessary to prevent excessive attack by alkaline solutions of $EDTA^{4-}$ (21). A combination of polyphosphate, chromate and Na_2H_2EDTA is recommended as a rust and scale preventing agent for automobile cooling systems (23).

Edwards and Roza (24) studied boiler scale prevention by using Na_4EDTA ("Verseme 100"), and reported that no appreciable decomposition of the free "Na_4EDTA" in solution occurs at temperatures below 400°F (200°C) and that the metal chelates are stable to 500°F (260°C). Unfortunately, the experimental evidence for this conclusion was not given nor was the evidence for the existence of free "Na_4EDTA" in 5 ppm or less at a pH of about 10.5 given. Edwards and Roza concluded that the application of Na_4EDTA in boilers which have maximum drum temperatures up to 500°F (260°C) would be feasible. Furthermore, since the free chelating agent and its metal chelates are reported to be nonvolatile below 500°F, the steam purity should not be affected in those cases where saturated steam might be taken from the drum and superheated to temperatures above 500°F. In this study, Na_4EDTA was continuously fed into the boiler feed water at a rate of 32.7 pounds per 24 hours; a quantity sufficient to inactivate all hardness in the boiler water and maintain a minimum pH of 10.0. Sufficient sodium sulfite was added to the feed water to maintain a minimum sulfite residual in the boiler of 10 ppm. Compared to a "disodium phosphate and caustic treatment" the treatment with the Na_4EDTA was competitive when savings on fuel and cleaning time were considered (24). The initial attempt by Edwards and Roza to clean a large deposit from an operating boiler was abandoned because it was found that the "Na_4EDTA was being carried over with the steam, presenting a possible source of contamination to the steam users". However, it was found that addition of sufficient chelating agent to inactivate the hardness of the makeup water prevented the formation of scale on the internal surfaces of a clean boiler. Since the calcium and magnesium chelates are soluble at the normal operating pH of a boiler, scale-forming components in the water would remain in solution and be removed through normal blowdown (24).

Decontamination of accumulated deposits of radioactive materials in pressurized water reactors can be accomplished by chemical means. Since the fundamental knowledge of the thermal stability of several potentially usable r ents was limited, Droll (25) tested aqueous solutions of six reagents, one of which was Na_2H_2EDTA, in stainless steel (AISI type 316 with type 304 stainless steel liners) autoclaves, for at least one hour at 300°F (149°C) and 400°F (204°C). All of the reagents decomposed fairly rapidly, with decomposition significantly more rapid at 400°F; citric acid, Na_2H_2EDTA and catechol appeared to be the most stable. After neutralization to the methyl red end-point, the amount of Na_2H_2EDTA present in solution was determined by titrating a portion of each sample, which had an excess of calcium nitrate added, with standard sodium hydroxide solution to the methyl red end-point. Titratable acidities were also determined by titrating a portion of each sample with standard sodium hydroxide solution to the phenolphthalein end-point. Solutions containing 120 and 250 ppm of Na_2H_2EDTA were reported to be completely decomposed within 30 min. at 400°F and a 60 ppm solution decomposed completely within 15 min. At 300°F, less than 50% of the Na_2H_2EDTA was left after 3 hours. Although there was no observable difference between the appearance of the samples taken from the solutions in the autoclaves and those of the reference solutions, it is quite conceivable that a product is formed which possesses the ability to chelate or complex metal ions to a reasonable degree. Droll did not attempt to discern the nature of the decomposition product or products, and his method of analysis could only qualitatively detect the presence of chelating products in solution.

Although the study of the effect of high temperatures and pressures on the stability of H_4EDTA has not yet been reported, Zittel (26) has studied the effect of gamma radiation on aqueous solutions of H_4EDTA. Under the conditions studied H_4EDTA was degraded by gamma radiation to the extent of about 1.4×10^{-9} millimoles per milliliter of solution irradiated per roentgen. Since the purpose of the work was to measure the effects of gamma radiation on H_4EDTA as it is used in analytical methods, no systematic study was made to identify the degradation products produced during gamma irradiation. A $1.2 \times 10^{-3}M$ solution of Na_2H_2EDTA which had been exposed to 10^6r, no longer contained the original chelating material as indicated by the titration with standard Th^{4+} solution. Infrared data showed that many changes occur in the H_4EDTA molecule as a result of the gamma irradiation, but no definite structures were reported. It was interesting to note that solutions of high pH are much less affected by radiation than those of low pH. Amperametric titration curves of irradiated Na_2H_2EDTA solutions titrated with VO^2 indicated that the degradation products still acted as chelating materials (26).

Thermal Behavior of Solid H_4EDTA and Its Metal Complexes

The thermal stability of $Na_2H_2EDTA \cdot 2H_2O$ has been extensively studied to determine the temperature at which the hydrated salt could be safely dried to constant weight (27). Although the hydrated salt loses water above 100°C, charring was reported above 150°C. Similar results have been reported by Dow Chemical Co. (28); the anhydrous compound Na_2H_2EDTA begins to decompose above 135°C and yields sodium carbonate as the residue at 750°C. Depending on the material studied, H_4EDTA is reported to be stable below the range 230° to 265°C (27,28, 29). The salts, however, exhibit weight losses at lower temperatures because of the evolution of hydrate-bound water (30). As Wendlandt noted, a strict comparison of decomposition temperatures reported by several workers cannot be made because of the different heating rates employed and the different inherent characteristics of the thermobalances and differential thermal analyzers used.

After the loss of the hydrate-water, the anhydrous sodium salt decomposes to ultimately yield sodium carbonate. Anhydrous $Na_2CaEDTA$ possesses excellent thermal properties; no weight losses are observed up to 337°C. Almost all of the free acids studied by Wendlandt (30) exhibit a single endothermic peak corresponding to the main decomposition of the compound. Very few peaks were noted that could be associated with the oxidation of carbonaceous material; the low temperature range employed may be the reason.

Langer and Gohlke (31) used mass spectrometric thermal analysis (MTA) to study the volatile products of thermal decomposition in a manner similar to differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Using MTA, $GeEDTA \cdot 2H_2O$ was found to decompose with liberation of water between 70°C and 100°C, and again between 160°C and 190°C. Carbon dioxide appeared between 270°C and 320°C, and above 380°C general rapid decomposition produced "small organic molecules such as ethylene, carbon monoxide, ammonia, nitrogen, etc." (31). Using $H_4EDTA \cdot 2H_2O \cdot HCl$, water and HCl were detected by MTA from room temperature to 100°C under reduced pressures of the system. At the point of complete decomposition, at a temperature greater than 200°C, a recording of the entire mass spectrum revealed the presence of CO_2, H_2O, NH_3, N_2, HCl, as well as ion fragments of minor intensity ranging from m/e 50 to m/e 150.

Although other reports of the thermal decomposition of H_4EDTA and its metal salts have added to a small background of available information (32,33,34,35), the work of Bhat and Iyer (36) is by far the most extensive study made to find out how various metal ions influence the thermal behavior as well as the mode of thermal decomposition of several solid $EDTA^{4-}$ complexes. The only effluent gases analyzed were CO_2 and CO and only in the case of the $CuH_2EDTA \cdot H_2O$ and $BiHEDTA \cdot H_2O$ complexes was the residue analyzed for nitrogen (95 percent nitrogen of the original complex remained in the residue). On the basis of their study, Bhat and Iyer (36) made four significant conclusions regarding the trends in the thermal behavior of <u>solid</u> metal-$EDTA^{4-}$ complexes heated to 700°C and higher.

(1) Although the thermal stabilities of the solid complexes studied are slightly better in nitrogen than in air, the behavior is similar except at higher temperatures where secondary reactions involving decomposition products and oxygen occur.

(2) The thermal stabilities of the complexes studied in a nitrogen atmosphere vary in the order Dy>Sb>Bi>Ni>Cu>Co>Ca≈Ba; the order does not suggest any possible correlation between decomposition temperature and stability constant or heat of complex formation in solution.

(3) The carboxyl groups in the complex decompose first and the ethylenediamine part of the molecule is comparatively more stable.

(4) Two modes of decomposition are observed for the degradation of carboxyl groups:

(a) decompositions occurring in two steps involving two carboxyl groups in each step, e.g., Co, Ca and Ba;

(b) all four carboxyl groups decompose in a single step, e.g., Bi, Sb, Cu, Ni and Dy. Such complexes are thermally more stable than complexes which decompose by the two step decarboxylation. Accordingly, Bhat and Iyer point out that the single step decarboxylation should occur when three or more carboxyls are coordinated to the metal, and that tetravalent complexes should lose all four carboxyl groups simultaneously, for example, complexes of Ge, Sn, Ti, Hf and Th (35). A summary of the modes of decomposition and the number of attached metal-carboxyl groups of the solid $EDTA^{4-}$ complex is shown in Table [illegible].

Conclusions and Future Work

A considerable amount of work has been reported on the use of ethylenedinitrilotetraacetic acid (H_4EDTA) and its metal salts as additives to boiler water. The additives appear to be quite beneficial in preventing corrosion of the boiler tubes and as a descaling agent. Most of the thermal decomposition investigations have been made on solid H_4EDTA and various solid metal-$EDTA^{4-}$ complexes. In general, the solids lose water and then decarboxylate in one or two steps, depending on the number of carboxyl groups attached to the metal; three or more attached carboxyl groups give rise to more thermally stable complexes which decarboxylate in a single step. Water, carbon monoxide, carbon dioxide, ammonia, nitrogen, ethylene, and "small organic molecules" with ion fragments of minor intensities ranging from m/e 50 to m/e 150 have been detected by mass spectrometric analysis of volatile decomposition products from $EDTA^{4-}$ derivatives. When solid H_4EDTA and its various metal salts were heated to temperatures of 700°C and above, the residues isolated consisted of metal, metal oxide, metal carbonate and carbon; the residue depended on the starting material and the gaseous atmosphere used during the degradation. After the loss of 3 CO_2 and 1 CO per mole of [illegible] and [illegible]·H_2O (corresponding to the loss of four carboxyl groups), analysis of the residue for nitrogen content showed that about [illegible] percent of the nitrogen originally present in the complex remained in the residue (8). This result indicates that the "ethylenediamine" part of the molecule is thermally more stable than the carboxyl groups. No studies have been reported on the nature of residues isolated after thermal decomposition of $EDTA^{4-}$ complexes in aqueous solution.

To fully understand the potential protection to Navy boilers by the lithium hydroxide - $EDTA^{4-}$ system, we must determine the rate at which aqueous solutions of $EDTA^{4-}$ thermally decompose, the identity of the volatile decomposition products and the identity and chelating properties of residual materials. If the residue is still a chelating agent, it should be more thermally stable than $EDTA^{4-}$ and lend itself to possible use under conditions of boiler operation. Since the identity of volatile products and residues from thermal decomposition of solid H_4EDTA and various salts will aid in the study of the aqueous solution decomposition, the thermal decomposition of solid H_4EDTA and Li_4EDTA is currently being investigated at this Laboratory. The rate of decomposition of Na_2H_2EDTA and Li_4EDTA in aqueous solution at 400°C is also being investigated. The solid phase and aqueous phase decompositions of $EDTA^{4-}$ are the topics of Part II and Part III, respectively, of this report.

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Table I

Metal-EDTA^{4-} Complexes: Formation Constants and Optimum pH of Formation for $M^{n+} + L^{4-} \rightleftharpoons ML^{n-4}$ or $M(OH)_n$ $L^{4-} \rightleftharpoons M(OH)_nL^{4-}$

Metal Ion	Log K_1 [a(4)]	pH for Optimum Formation	Crystal Ionic Radii[b] (Å)
Li^+	2.8	>12	0.68
Na^+	1.7	>12	0.97
Mg^{2+}	8.7	≤11	0.82
Ca^{2+}	10.6	10.7	0.99
Fe^{2+}	14.3	5	0.74
Fe^{3+}	25.1	1	0.64
$Fe(OH)_2$	8.2[c]	-	-
$Fe(OH)_3$	-7.0[c]	-	-

[a] 20°C in 0.1M KCl.

[b] Weast, R.C. and Selby, S.M., "Handbook of Chemistry and Physics," 47th edition, The Chemical Rubber Co., Cleveland, Ohio, 1966, p. F124.

[c] Calculated values from data given in reference (4).

Table II

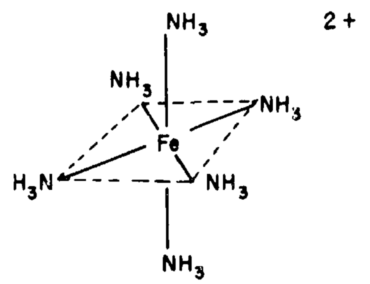
Mode of Decomposition of Solid Metal-ethylenedinitrilotetraacetates

Metal Salt of H_4EDTA	No. of Steps in Decarboxylation	No. of Carboxyl Groups Attached to Metal	Reference
$Na_2CaEDTA$	1	4	30
CaH_2EDTA	2	2[a]	30
BaH_2EDTA	2	2[b]	30
$CoH_2EDTA \cdot 3H_2O$	2	2	30
$DyHEDTA \cdot 2H_2O$	1	3	30
$BiHEDTA \cdot H_2O$	1	3	30
$SbHEDTA$	1	3	30
$NiH_2EDTA \cdot H_2O$	1	3[b]	30
$CuH_2EDTA \cdot H_2O$	1	3[b]	34
$GeEDTA \cdot 2H_2O$	1	4	34
$SnEDTA \cdot H_2O$	1	4	34
$TiEDTA \cdot H_2O$	1	4	34
$HfEDTA \cdot 4H_2O$	1	4	34
$ThEDTA \cdot 2H_2O$	1	4	34

[a] Two protons associated with two carboxyl groups.

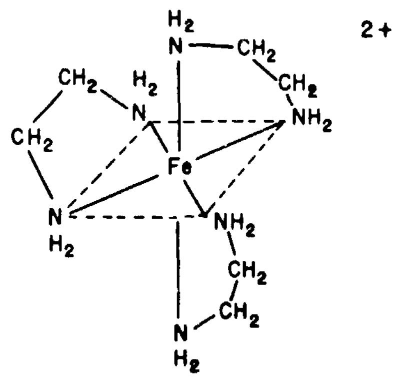
[b] One proton associated with a carboxyl group and the other to a water molecule.

1. MONODENTATE LIGAND: AMMONIA



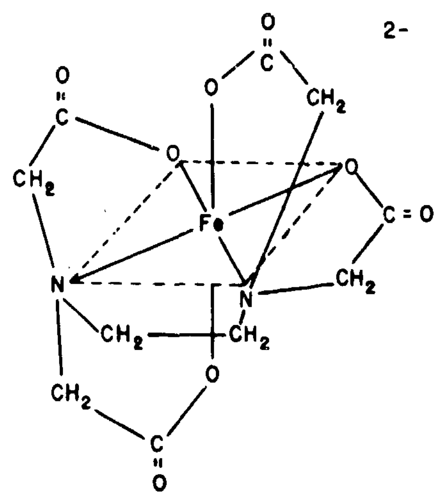
$pK_1 = 1.4$

2. BIDENTATE LIGAND: ETHYLENEDIAMINE



$pK_1 = 4.34$

3. HEXADENTATE LIGAND: ETHYLENEDINITRILOTETRAACETATE



$pK_1 = 14.3$

Fig. 1 - The Chelate Effect. Relationship between the formation constants of iron(II) complexes and the number of ligand-attachment points.

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13. ABSTRACT

From the standpoint of boiler-wall corrosion prevention, preliminary studies at this Laboratory and at the Naval Ship Research and Development Center have indicated that a chelating agent, ethylenedinitrilotetraacetic acid (H_4EDTA), in conjunction with lithium hydroxide is preferable to the low-phosphate control treatment presently being used by the Navy. To elucidate the corrosion-inhibition mechanism in the lithium hydroxide-$EDTA^{4-}$ system, we must know the rate and the mechanism of $EDTA^{4-}$ decomposition in aqueous solutions under conditions of high-pressure boiler operations. As a background for investigations at this Laboratory of the solid phase and solution phase decomposition of $EDTA^{4-}$ at high temperatures, the available literature has been examined and pertinent facts related to the lithium hydroxide-$EDTA^{4-}$ system are reported. The general properties of $EDTA^{4-}$ chelates are reviewed first. Although a considerable amount of information is available related to the use of alkali-metal hydroxides and $EDTA^{4-}$ solutions for hard-scale removal and corrosion prevention, no studies have been reported on decomposition products from aqueous $EDTA^{4-}$ solutions heated under pressure to high temperatures. The qualitative investigations of the thermal decomposition of solid H_4EDTA and its metal salts fail to fully identify the volatile products and residues formed at temperatures near those of boiler operations.

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Thermal stability of chelates						
Ethylenedinitrilotetraacetic acid						
Salts of ethylenedinitrilotetraacetic acid						
EDTA						

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